STRUKTUR UND AKTIVIERUNG DER MOLEKEL DES PHOSGENS

EINE ANALYSE AUF GRUND DES ULTRAVIOLETTEN ABSORPTIONSSPEKTRUMS DES DAMPFES

INAUGURAL-DISSERTATION

ZUR

ERLANGUNG DER PHILOSOPHISCHEN DOKTORWÜRDE

VORGELEGT DER

PHILOSOPHISCHEN FAKULTÄT II

DER

UNIVERSITÄT ZÜRICH

VON

OWEN RHYS HOWELL

AUS

MANCHESTER (ENGLAND)

BEGUTACHTET VON HERRN

PROF. DR. V. HENRI

1930

Jesse Broad & Co. Ltd., Stretford Road, Old Trafford, Manchester

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CURRICULUM VITAE

I, OWEN RHYS HOWELL, of 14 Kent Road West, Victoria Park, Manchester, England, was born at Narberth, in the County of Pembroke, South Wales, on 22nd February, 1892. I received my early education at the Church of England School and the County School in that town. I then entered the University College of Wales, Aberystwyth, where I graduated B.Sc. (Wales) with first class honours in Chemistry. I spent the next two years in research with Professor Alex. Findlay, and was elected University Scholar in Chemistry and Scholar of the Royal Exhibition of 1851.

I was proceeding to Germany for further research experience when war was declared. After serving for two years as Lieutenant in the London Regiment, I was transferred to reserve for chemical warfare research, and spent two years with the South Metropolitan Gas Co., and another two with the Mond Nickel Co.

In order to resume academic work, I returned to Aberystwyth in 1920, as Assistant Lecturer and Demonstrator in Chemistry under Professor B. Mouat Jones, D.S.O., and obtained the Ph.D. (Wales). Proceeding to Cambridge (Emmanuel College), I spent the next two years in research in the University Physical Chemistry Laboratories directed by Professor T. M. Lowry, C.B.E., F.R.S., and graduated Ph.D. (Cantab). I would like to place on record my thanks to the Commissioners of the Royal Exhibition of 1851, and especially the Secretary, Mr. Evelyn Shaw, for their kindness in suspending the scholarship to enable me to resume my studies at this time, and in extending it for a third year. This year I spent at Zürich researching with Professor Victor Henri, and the work I then did, and subsequently completed, is the subject of the present thesis.

After leaving Zürich, I was for two years Lecturer in Physical Chemistry at the University College, Dundee, University of St. Andrews, under Professor Alex. McKenzie, F.R.S., and since then have been Lecturer in Applied Chemistry in the University and College of Technology, Manchester, first under Professor F. L. Pyman, F.R.S., and now Professor J. Kenner, F.R.S.

To

MY WIFE

THE STRUCTURE AND ACTIVATION OF THE PHOSGENE MOLECULE.

BY

V. HENRI AND O. R. HOWELL.

[*Reprinted from the* Proceedings of the Royal Society, A, Vol. 128.]

The Structure and Activation of the Phosgene Molecule. Part I.—*General Introduction—Predissociation of Molecules.*

By Victor Henri, Professor of Physical Chemistry at the University of Zürich, and Owen Rhys Howell, Lecturer at the College of Technology, University of Manchester.

(Communicated by T. M. Lowry, F.R.S.—Received November 14, 1929.—Revised March 31, 1930.)

The study of diatomic molecules is already very advanced. By applying the principles of wave mechanics a number of authors, especially Hund, Heitler, London, Mulliken, Herzberg, Wigner and Witmer, have developed the theory of the conditions of formation, of electronic activation, and of different types of dissociation of diatomic molecules. They have also established relations between the electronic terms of atoms and those of related molecules, and have thus succeeded in arranging the terms of molecular spectra in a manner analogous to that for atomic spectra.

The experimental researches during recent years of Mulliken, Mecke, Hund, Diecke, Franck and his school, Hulthen, Birge, Hopfield, Richardson, Curtis, Johnson, Herzberg and many others have established a very exact knowledge of the structure of spectra of diatomic molecules.

The study of polyatomic molecules, however, is still in its infancy. Theory has not yet been developed and few complete experimental investigations have been made. The mathematician is in need of sufficient experimental basis for attacking theoretically the problem of the polyatomic molecule.

The study of triatomic molecules has been attempted; the ultra-violet absorption spectra of chlorine dioxide, sulphur dioxide and carbon disulphide having been measured by several observers. In this laboratory, the absorption spectrum of SO_2 and its analysis is being investigated by Motschan and that of CS_2 by Koffler. The interest of this simultaneous study is that these two molecules belong to entirely different types. Sulphur dioxide is a *triangular molecule* having a large electric moment of $\mu = 1 \cdot 61 \times 10^{-18}$ according to Zahn.* Carbon disulphide, on the other hand, has the same structure as CO_2; it is a *linear molecule* having a zero electric moment as found by Hoejendahl† from the experiments of Pohrt.‡ The same conclusion has been reached by Debye in his recent book§ and in a private communication.

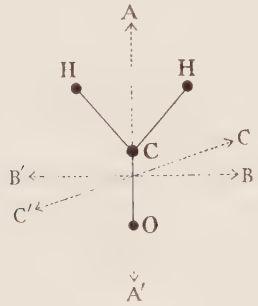
The ultra-violet absorption spectra of other triatomic molecules have also been examined by different observers but the spectra are very complex and no complete analysis has been made.

Among tetra-atomic molecules, formaldehyde has been studied by Henri and Schou.|| This has been shown to be a Y-shaped molecule and may be written . The ultra-violet absorption spectrum of this compound consists of a series of vibration bands, each of which is composed of a large number of very fine lines which correspond to a double rotation state of the molecule.¶ The rotation lines are very sharp and easily measured, so that it has been possible to make a complete analysis of the rotation spectrum of this tetra-atomic molecule, and obtain the values of the moments of inertia.

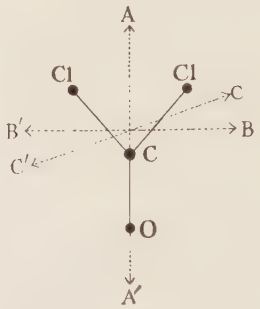
Simultaneously, two other compounds of the same class of Y molecules have also been studied in this laboratory, namely, phosgene and thiophosgene . These molecules have a structure quite analogous to that of formalde-

* 'Phys. Rev.,' vol. 27, p. 455 (1926).
† 'Diss. Kopenhagen,' 1928.
‡ 'Ann. Physik,' vol. 42, p. 569 (1913).
§ Debye, 'Polare Molekeln,' Leipzig, 1929.
|| 'Z. Physik,' vol. 49, p. 774 (1928).
¶ Henri and Schou, 'Nature,' vol. 118, p. 225 (1926).

hyde, but they differ in possessing far greater moments of inertia. The rotation spectrum therefore consists of lines extremely close together, the distance between them being of the same order as the breadth of the lines themselves, so that it is impossible to measure them.



Formaldehyde.



Phosgene.

Formaldehyde possesses three moments of inertia : J about the axis AA′, K about the axis BB′, and L about the axis CC′. The third moment, L, is approximately equal to K. The values of these have been calculated from the rotation spectrum and found to be : $J_0 = 1{\cdot}38 \times 10^{-40}$; $K_0 = 23 \times 10^{-40}$. The distance between the hydrogen atoms is $1{\cdot}3 \times 10^{-8}$ cm. and between C and O $1{\cdot}2 \times 10^{-8}$ cm.

Phosgene also has three moments of inertia, but L is quite different from K. Since the atoms are all in one plane J + K = L.

The recent researches of Debye, Bewilogua and Ehrhardt,* on the scattering of X-rays by carbon tetra-chloride vapour, have established that the distance between neighbouring chlorine atoms in the molecule of carbon tetrachloride is $3{\cdot}1 \times 10^{-8}$ cm. Assuming that the chlorine atoms in the phosgene molecule are separated by the same distance, then the moment of inertia about AA′ is :

$$J = 2 \times 35 \times 1{\cdot}65 \times 10^{-24} \times (1{\cdot}55)^2 \times 10^{-16} = 266 \times 10^{-40},$$

and the other two moments of inertia, K and L, must be still greater.

The rotation spectrum (branches P and R) is approximately represented by the formula :

$$\frac{1}{\lambda} = \nu_0 \pm (B_0 + B')\, m + Cm^2$$

* ‘ Phys. Zeit.,’ vol. 30, p. 84 (1929).

where

$$B_0 = \frac{h}{8\pi^2 C}\left(\frac{1}{J_0} - \frac{1}{K_0}\right) = 27{\cdot}7 \times 10^{-40}\left(\frac{1}{J_0} - \frac{1}{K_0}\right)$$

and

$$B' = \frac{h}{8\pi^2 C}\left(\frac{1}{J'} - \frac{1}{K_0}\right) = 27{\cdot}7 \times 10^{-40}\left(\frac{1}{J'} - \frac{1}{K_0}\right).$$

Then, neglecting $\frac{1}{K_0}$ (since K_0 is very large)

$$B_0 + B' = \frac{2 \times 27{\cdot}7 \times 10^{-40}}{266 \times 10^{-40}} = 0{\cdot}2 \text{ cm.}^{-1}.$$

The spectrum due to the rotation about the axis AA′ is therefore composed, for each branch, of lines separated by less than 0·2 cm.$^{-1}$. The spectrum of the rotation about the axes BB′ and CC′ is composed of lines still more closely packed.

The breadth of the bands in the finest region of the absorption spectrum of phosgene is about 2 cm.$^{-1}$, so that in this small interval there are superposed more than 20 rotation lines. It is therefore evidently impossible to observe separately the rotation lines of a molecule-like phosgene. The superposition of the rotation lines produces a broadening of the vibration bands. Each band is degraded towards the visible and has a sharp edge towards the ultra-violet. This signifies that the moment of inertia is augmented by electronic activation of the molecule; in other words, the distance between the vibrating atoms increases. This can be very readily seen in fig. 1 which is a micro-

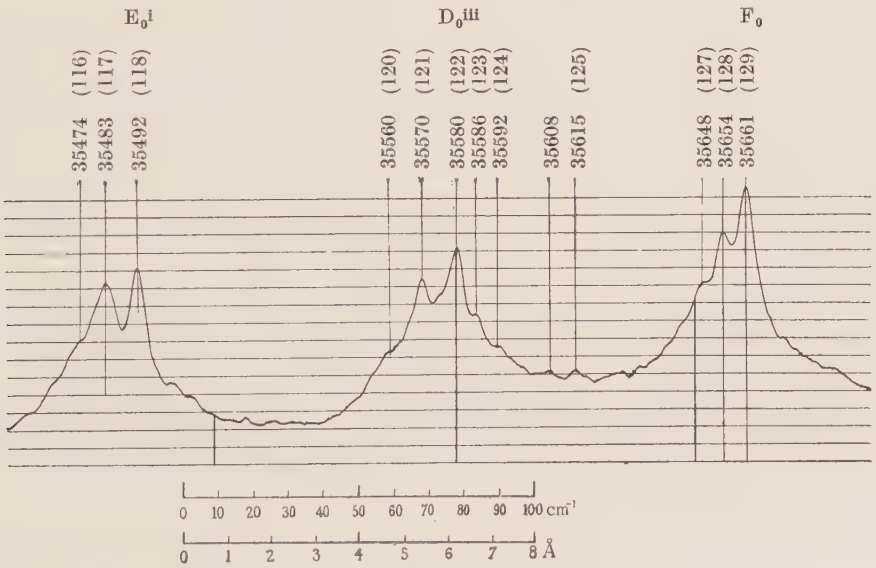


Fig. 1.

photogram of a small portion of the absorption spectrum of phosgene. This portion between $\lambda = 2820$ and 2800 Å. contains three groups of bands :—

No. 129 $\frac{1}{\lambda} = 35661$	No. 122 $\frac{1}{\lambda} = 35580$	No. 118 $\frac{1}{\lambda} = 35492$
,, 128 $\frac{1}{\lambda} = 35654$	,, 121 $\frac{1}{\lambda} = 35570$	,, 117 $\frac{1}{\lambda} = 35483$
,, 127 $\frac{1}{\lambda} = 35648$	,, 120 $\frac{1}{\lambda} = 35560$	,, 116 $\frac{1}{\lambda} = 35474$

The ultra-violet side falls more abruptly than the red side of each band. The rotation lines cannot be distinguished in this spectrum ; there must be more than 40 lines between the bands 129 and 128.

The absorption spectrum obtained with polyatomic molecules having large moments of inertia is therefore a pure vibration spectrum with a series of states of electronic activation, and its investigation involves an analysis of this vibration spectrum. The study of infra-red and of Raman spectra shows that all polyatomic molecules possess several fundamental frequencies of atomic vibration, which are designated α_0, β_0, γ_0, ..., for the normal molecule and α' β', γ', ..., for the activated molecule.

The entire spectrum is then represented by the formula :

$$\frac{1}{\lambda} = \nu_0 + p'\alpha'(1 - x'p') - p_0\alpha_0(1 - x_0p_0) + q'\beta'(1 - y'q') - q_0\beta_0(1 - y_0q_0) + \ldots,$$

where p_0, q_0 ... and p', q' ... are vibration quantum numbers for the normal and activated molecule respectively, and x, y, ... are correction factors for non-harmonicity of the vibrations. This formula is certainly incomplete. There must also be terms corresponding to the mutual influences of the different vibrations in the molecule, but there is not yet sufficient experimental data available for the determination of the form of these additional terms. We hope to obtain these terms by the accurate study of the vibration spectra of SO_2 and CS_2.

The coefficients x, y, ... are approximately inversely proportional to the moments of inertia of the molecule ; these moments are very large, consequently the collection for non-harmonicity in polyatomic molecules containing heavy atoms will generally be very small. This is true for phosgene, so that the formula for the vibration spectrum simplifies to

$$\nu = \nu_0 + p'\alpha' - p_0\alpha_0 + q'\beta' - q_0\beta_0 + \ldots.$$

which may also be written for convenience in calculation

$$\nu = \nu_0 + (p' - p_0)\alpha' + p_0(\alpha' - \alpha_0) + (q' - q_0)\beta' + q_0(\beta' - \beta_0) + \ldots.$$

The primary difficulty in the study of a vibration spectrum is to account for the observed bands in terms of this formula. In analysing such a spectrum, the problem consists in finding which vibration periods are due to the various atoms, both in the normal molecule and in the excited molecule.

The first important criterion in deciding whether certain intervals between the absorption-bands are due to the vibration in the normal molecule or in its excited state, is whether they occur in the direction of increasing or of decreasing wave-length. If a long series of intense bands occurs at regular intervals from a given origin towards the ultra-violet, this period may be ascribed with certainty to the atoms in the electronically excited molecule. If, on the other hand, a small number of bands of lower intensity is found distributed at regular intervals from each intense band towards the red, then these intervals are due to vibration periods of the atoms in the normal molecule.

The vibration periods of the atoms in the normal molecule can be also obtained from the infra-red vibration spectra. Unfortunately, these spectra have not been well elucidated and they cannot be measured with great precision since the bands are generally very broad. Very accurate measurements of infra-red absorption spectra have recently been made by Barnes.†

The same information can, however, be obtained from the Raman spectra, which gives the different vibration frequencies of the atoms in the normal molecule with great exactitude. Consequently the study of the ultra-violet absorption spectrum of a compound should always be made in conjunction with that of its Raman spectrum. This procedure has been adopted in this laboratory and has been applied with very satisfactory results to the study of the ultra-violet spectrum of chlorobenzene by Langseth,‡ of carbon disulphide by Koffler, of benzene and indene by Shapiro, and of benzaldehyde by Almasy. The present communication includes an account of the application of a knowledge of the Raman spectrum of phosgene to the elucidation of its ultra-violet absorption spectrum.

The study of the vibration spectrum gives important information regarding the structure of the molecule and the conditions of its stability.

For diatomic molecules Franck has shown that it is possible to calculate from the convergence of the vibration spectrum and from the values of the coefficients of non-harmonicity, x_0 and x', the energy of dissociation of a molecule AB into two normal atoms and also into activated atoms A* and B*.

† 'Nature,' vol. 124, p. 300 (1929).
‡ 'Nature,' vol. 124, p. 92 (1929).

This method has been recently applied in the study of the molecule of sulphur monoxide SO.*

For polyatomic molecules, this criterion of the convergence of the vibration terms cannot be employed, or, rather, has not yet been applied. The stability of such molecules can, however, be deduced from a study of two characteristics of the spectra.

1. *Deformability.*—A frequency of vibration α_0 in the normal molecule becomes α' in the activated molecule. As a general rule α' is less than α_0 and this signifies that the distance between the vibrating masses is increased by electronic activation.

The binding force or the quasi-elastic force between the vibrating atoms is proportional to $\mu\alpha^2$, where μ is the electric movement of the molecule. Relative values of the "deformability" of molecules are given by the expression $(\alpha_0^2 - \alpha'^2)/\alpha^2$.

Kuhn† has shown from a study of the absorption spectra of chlorine, bromine and iodine that the value of $\mu\alpha_0^2$ is very exactly proportional to the heat of dissociation of Cl_2, Br_2 and I_2. The same result has been obtained by Rosen‡ for the molecules O_2, S_2, Se_2 and Te_2.

Another general relation has been found by Rosen and Mecke and extended by Henri between the vibration frequencies and the atomic numbers (Z_1, Z_2) of vibrating atoms in a diatomic molecule, namely, that the expression $\alpha_0^2 Z_1 Z_2$ is quite constant for a large number of different molecules. No similar relation has as yet been found for polyatomic molecules.

2. *Predissociation.*—It has been shown§ that, for a great number of substances, the vibration bands become diffuse at a certain wave-length and increase in breadth the further they occur towards the ultra-violet. This broadening of the vibration bands and disappearance of the quantisation of molecular rotation are accompanied by a number of changes in the properties of the molecule‖ :—

* Henri and Wolff, 'J. Physique,' vol. 10, p. 81 (1929). This memoir also contains an historic account of vibration spectra and their relation to the different types of dissociation of molecules. See also Henri, "Structure des molécules et spectre de bandes." 'Réunion Internationale de Chimie Physique,' Paris, 1928.

† 'Z. Physik,' vol. 39, p. 77 (1926).

‡ 'Z. Physik,' vol. 43, p. 121 (1927).

§ Henri and Teves, 'Nature,' vol. 114, p. 894 (1924); Henri, 'Structure des molécules, Paris, 1925, p. 82; Henri and Schou, 'Z. Physik,' vol. 49, p. 818 (1928).

‖ For further details see Henri and Wurmser, 'J. Physique,' vol. 8, p. 289 (1927); Hemptine, 'J. Physique,' vol. 9, p. 357 (1928).

(*a*) The vibration frequency in this region becomes less, signifying an increase in the distance between the vibrating masses; the molecule becomes *labile*.

(*b*) The fluorescence excited by the light in the region of the diffuse bands is very feeble or, indeed, entirely absent.

(*c*) The molecule becomes chemically active.

(*d*) The limiting wave-length at which these diffuse bands appear is displaced towards the red on raising the temperature, and the greater the molecular specific heat of the molecule, the greater the displacement. ("Thermal predissociation.")

Under the influence of light and also of heat, the molecule passes to a new state, intermediate between that of the normal molecule and the dissociated molecule, and this state has been given the name *predissociation* (Henri, *loc. cit.*).

Many authors (Kronig, Wentzel, Bonhoeffer, Rice, Franck, Sponer, Henri, etc.) have given a theory of the predissociation of molecules. The spectrum becomes diffuse because of a great diminution in the duration of life of the active molecule, which becomes of the same order of magnitude as the period of rotation. The great decrease in the life of the molecule occurs in general when, by the superposition of atomic vibration, the activated molecule acquires an energy level greater than that corresponding to the dissociation of the normal molecule into normal atoms, and also when the molecule, in a certain state of vibrational activation, can return to the initial state in two or more different ways; this is a sort of Auger phenomenon.*

The experimental studies made in Zürich on the photochemical decomposition of benzaldehyde† and on acetaldehyde,‡ have demonstrated the remarkable agreement between the energy of dissociation of the molecule and the wave-length at which the spectrum begins to become diffuse.

The primary photochemical reactions are

$$C_6H_5CHO + h\nu \rightarrow C_6H_5 + CO + H$$

$$CH_3CHO + h\nu \rightarrow CH_3 + CO + H.$$

The corresponding energies calculated from thermochemical data are—155780 and — 93300 cals. respectively. These energies correspond to the wave-

* Bonhoeffer, 'Z. Phys. Chem.,' vol. 134, p. 337 (1929); Franck and Sponer, "Göttingen Nachr.," 1929.

† de Hemptine, 'J. Physique,' vol. 9, p. 356 (1928).

‡ Smith, appearing in 'Z. Phys. Chem.,' 1930.

lengths $\lambda = 2461$ Å. and 3050 Å., whilst the region of predissociation is found to begin at room temperature with benzaldehyde at $\lambda = 2460$ Å. and with acetaldehyde at $\lambda = 3054$ Å.

Similarly, good agreement is found for sulphur vapour. S_2 gives an absorption spectrum composed of very fine lines which become diffuse abruptly at $\lambda = 2792$ Å. The energy of dissociation of $S_2 = 2S$ at 400°–600° is 103,500 cals.* which corresponds to $\lambda = 2760$ Å. The determination of the energy of dissociation is not very accurate; the agreement between the observed and calculated limits of predissociation is therefore satisfactory.

Benzaldehyde vapour (de Hemptine) and acetaldehyde vapour (Smith) at room temperature undergo no photochemical decomposition with light of $\lambda = 2750$ and 3050 Å. respectively, and the absorption bands at these wave-lengths are sharp; at 200°, however, photochemical decomposition does occur and the absorption bands become broad and diffuse in these regions.

Diffuse absorption bands are therefore characteristic of a special chemical sensitivity of the molecule. Consequently, it is possible by determining the limiting wave-length at which the bands in the absorption spectrum begin to become diffuse, to predict that photochemical action on the molecules will begin only with light of shorter wave-length and to calculate the energy of primary dissociation of the molecule.

The study of phosgene is of general interest, because the molecule contains a carbonyl group, CO. The absorption spectra of different molecules containing a CO group have been studied in this laboratory by Lardy, Grossmann, Light, Luthy, Almasy, de Hemptine, Schou and Henri; the absorption spectrum of carbon-monoxide itself has also been studied (Henri and Schou, 'C.R.,' Paris).

The presence of the carbonyl group in a molecule always produces an absorption band in the middle of the ultra-violet (between 3200 and 2600 Å.). If the compound is in the vapour state, the spectrum is composed of a large number of fine bands distributed at regular intervals. Towards the ultra-violet these bands become broad and diffuse, at a certain point, corresponding to a predissociation of the molecule.

All these molecules undergo photochemical and thermal decomposition, with production of carbon monoxide, hydrocarbons and hydrogen. For phosgene, the same decomposition gives CO and chlorine.

The exact mechanism of the separation of CO from the rest of the molecule is as yet not fully explained. The carbon atom in carbon monoxide is probably

* Budde, 'Z. Anorg. Chem.,' vol. 79, p. 169 (1912).

in a different electronic state from that of the carbon atom in molecules like aldehydes, ketones or phosgene. In carbon monoxide, it is very probable (Johnson) that the carbon atom is in its normal state, that is a ^3P state, but in a molecule like phosgene, the carbon atom is tetravalent and is in the activated state ^5S. The same must be true of the carbon atom in aldehydes and ketones, so that the carbonyl group in all these molecules is different in its electronic configuration from carbon monoxide itself.

Confirmation of this conclusion is found in the measurements of the polarity of carbon monoxide and of molecules containing the carbonyl group. The electric moment of carbon monoxide is $\mu = 0{\cdot}10 \times 10^{-18}$ *; that of several ketones is $\mu = 2{\cdot}7 \times 10^{-18}$,† the influence of substitution being very small (thus for $CH_3 . CO . CH_3$ $\mu = 2{\cdot}71$ and for C_3H_7 $\mu = 2{\cdot}73$). The large value of the polarity of ketones and aldehydes is determined by the carbonyl group; this high value of μ must therefore be explained by the difference in the distribution of electrons in the carbon atom of carbonyl and of carbon monoxide.

The comparative study of the vibrational frequencies of different types of molecules containing the carbonyl group will give important results concerning the mutual influence of atoms in the molecule. A comparison of the different carbonyl compounds is given later.

A further point of general interest which arises from a study of the absorption spectrum of phosgene is the possibility of determining the isotope effect for polyatomic molecules. Mulliken‡ and later Mecke and many other observers, especially Birge, Elliott and Curtis, have obtained a rotational and vibrational isotope effect for many different diatomic molecules. For the chlorine molecule, Elliott§ has measured the vibrational isotope effect corresponding to the molecules $Cl^{35}Cl^{35}$, $Cl^{35}Cl^{37}$ and $Cl^{37}Cl^{37}$. He observed that the separation corresponding to the first two isotopes is equal to $9{\cdot}6 \pm 0{\cdot}2$ cm.$^{-1}$ for the band $\nu_0 = 19389$ cm.$^{-1}$.

If the vibrational energy is represented by $E_p = h\alpha cp\,(1 - xp)$, then the separation for the two isotopes is :—

$$\nu_1 - \nu_2 = (1 - \rho)\,(\alpha' p' - \alpha_0 p_0) - (1 - \rho^2)\,(\alpha' x' p'^2 - \alpha_0 x_0 p_0^2),$$

where

$$\rho^2 = \frac{\mu_1}{\mu_2} = \frac{m' + m_2}{m' + m_1}\frac{m_1}{m_2},$$

* Zahn and Miles, ' Phys. Rev.,' vol. 32, p. 497 (1928).

† Wolf, ' Z. Phys. Chem.,' B, vol. 2, p. 39 (1929).

‡ ' Phys. Rev.,' vol. 25, p. 119, and vol. 26, pp. 1, 319 (1925).

§ ' Roy. Soc. Proc.,' vol. 123, p. 629 (1929).

m' being the mass of A and m_1 and m_2 the masses of B_1 and B_2 respectively in the molecules AB_1 and AB_2.

By assuming for the chlorine molecule $\alpha_0 = 565$ cm.$^{-1}$ and $\alpha' = 120$ cm.$^{-1}$, $p_0 = 2$ and $p' = 18$, Elliott obtained a value for the separation of isotopes very closely equal to the observed.

The theory of the isotope effect has recently been developed by Curtis and Patkowski* from a very accurate experimental study of the absorption spectrum of iodine monochloride. The separation between the bands of ICl^{35} and ICl^{37} increases for the first successive values of the vibration quantum numbers of the activated molecule, then attains a maximum and falls for higher values of vibration quanta.

This theory cannot be directly extended to polyatomic molecules. The frequency of vibration in these molecules is not dependent on the masses of only two atoms, but is influenced by those of the other atoms; and the different fundamental vibrations in the molecule are not independent, but are mutually influenced by those of all the other atoms. The theoretical treatment of the isotope effect in polyatomic molecules cannot be developed, because there is no available data on the laws of the mutual influence of the different atoms in the molecule. We can only assume that the separations due to the isotope effect will be greater for certain vibrations than for others. For example, in the molecule of phosgene Cl Cl, it may be supposed that there are

three fundamental frequencies corresponding to vibrations between (1) Cl and Cl; (2) Cl and C; and (3) C and O. If these vibrations were totally independent, we should observe triplets for the bands corresponding to (1), doublets for the bands corresponding to (2) and singlets for the bands corresponding to (3), and the separations should be different for (1) and (2). These three sorts of bands are actually found in the absorption spectrum. Thus, for example, in the microphotogram (fig. 1) of a portion of the phosgene spectrum, can be seen very clearly the triplet No. 129, 128, 127 with separations 35661 — 35654 = 7 cm.$^{-1}$ and 35654 — 35647 = 7 cm.$^{-1}$; band No. 122 shows a well-developed doublet with separation 35580 — 35570 = 10 cm.$^{-1}$, and there is indication of a third band 35560. The same appearance is presented by band No. 118, which is a doublet 35492 — 35483 = 9 cm.$^{-1}$, with indication of a third component 35474.

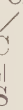
* 'Faraday Trans.,' vol. 25, p. 725 (1929).

The relative intensities of the components of these triplets correspond quite well with the abundance of the different isotope molecules. The variation of the separation between the isotopic bands for successive quantum numbers is, however, not so simple as in diatomic molecules ; it is therefore not possible as yet to calculate from these separations the absolute values of the vibration quanta, but it may be observed that the separation increases from the red to the ultra-violet end of the spectrum.

An analogous isotope effect for polyatomic molecules was recently observed in the absorption spectrum of chlorine dioxide by Goodeve and Stein.* The separation does not seem to be the same as for a simple diatomic molecule. It is therefore of great interest to study the isotope effect for different sorts of polyatomic molecules.

In this laboratory, Langseth† has observed a doubling of certain bands with chlorobenzene which is probably due to the isotope effect produced by the chlorine atom.

A similar isotope effect to that of phosgene is shown in the absorption spectrum of thiophosgene Cl Cl, which we have studied. This spectrum will be



published in a further paper.

* ' Faraday Trans.,' vol. 25, p. 738 (1929).
† ' Nature,' vol. 124, p. 92 (1929).

The Structure and Activation of the Phosgene Molecule. Part II.—*The Raman Spectrum of Phosgene.*

By Victor Henri, Professor of Physical Chemistry at the University of Zürich, and Owen Rhys Howell, Lecturer at the College of Technology, University of Manchester.

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The vessel in which the phosgene was contained for illumination was a glass tube 3 cm. diameter and 10 cm. long, closed at one end and ending at the other in a " tail " bent at right angles. The tail had a bulb of about 25 c.c. capacity to allow for subsequent expansion of the liquid after filling at low temperature, and it was coated with black wax to prevent reflection from this end of the vessel.

This Raman tube was filled in the following way. A stream of phosgene from a bomb (supplied by Messrs. Siegfried, of Zofingen) was led through a glass coil cooled in a freezing mixture of ice and salt. The condensed phosgene was received in a bulb of about 120 c.c. capacity cooled in ether and carbon dioxide ice. The bulb was joined to the Raman tube and a side tube was provided for evacuation. When a sufficient quantity of liquid had been collected, the receiving bulb was sealed off from the condenser coil, the two bulbs were evacuated through calcium chloride tubes by means of a water-pump and the side tube was sealed off. The Raman tube was then cooled in alcohol and carbon dioxide ice and the receiving bulb allowed to warm slowly, so that the phosgene distilled over quietly without ebullition. When the requisite amount was present, the tube was sealed off. The liquid produced in the initial condensation was somewhat cloudy but on redistillation into the Raman tube it was obtained perfectly clear.

The method of obtaining the spectrum was as follows. A wooden box ($35 \times 15 \times 20$ cm.) was provided with two glass windows; one (7×3 cm.) at one side and the other (3 cm. diameter) in front. The Raman tube was suspended in the box parallel to the rectangular window and in line with the circular one. The tube was illuminated through the side window by a mercury-vapour lamp. Pieces of highly polished aluminium foil were bent round the lamp to the window and round the tube to the window to serve as reflectors and so secure as great a concentration of light as possible in the tube. A stream of

cold water was kept flowing through the box and a jet of dry air was directed against the circular window to prevent deposition of moisture.

The emergent light was focussed by two lenses on to a spectrograph and an exposure of 26 hours was made. Details of the spectrum are given in Table I.

Table I.—Raman Spectrum of Phosgene.

Intensity.	$\frac{1}{\lambda}$	$\Delta\frac{1}{\lambda}$ from the Hg line :—	
		$\lambda = 4358{\cdot}6$ A. $\frac{1}{\lambda} = 22937$ cm.$^{-1}$.	$\lambda = 4046{\cdot}9$ A. $\frac{1}{\lambda} = 24703$ cm.$^{-1}$.
	cm.$^{-1}$.	cm.$^{-1}$.	cm.$^{-1}$.
3	22370	567	—
1	22494	443	—
2	22648	289	—
3	24137	—	566
1	24259	—	444
2	24412	—	291

Mean values : $a = 567 \pm 8$ cm.$^{-1}$. $b = 443$. $c = 290$.

There are therefore three vibration frequencies corresponding to wave-lengths 17·6, 22·5 and 34·4 μ. The infra-red absorption spectrum has not been measured for long wave-lengths, so that it is not possible to compare the Raman spectrum with it.

The Structure and Activation of the Phosgene Molecule. Part III.— *A Study of the Ultra-Violet Absorption Spectrum of Phosgene Vapour.*

By Victor Henri, Professor of Physical Chemistry at the University of Zürich, and Owen Rhys Howell, Lecturer at the College of Technology, University of Manchester.

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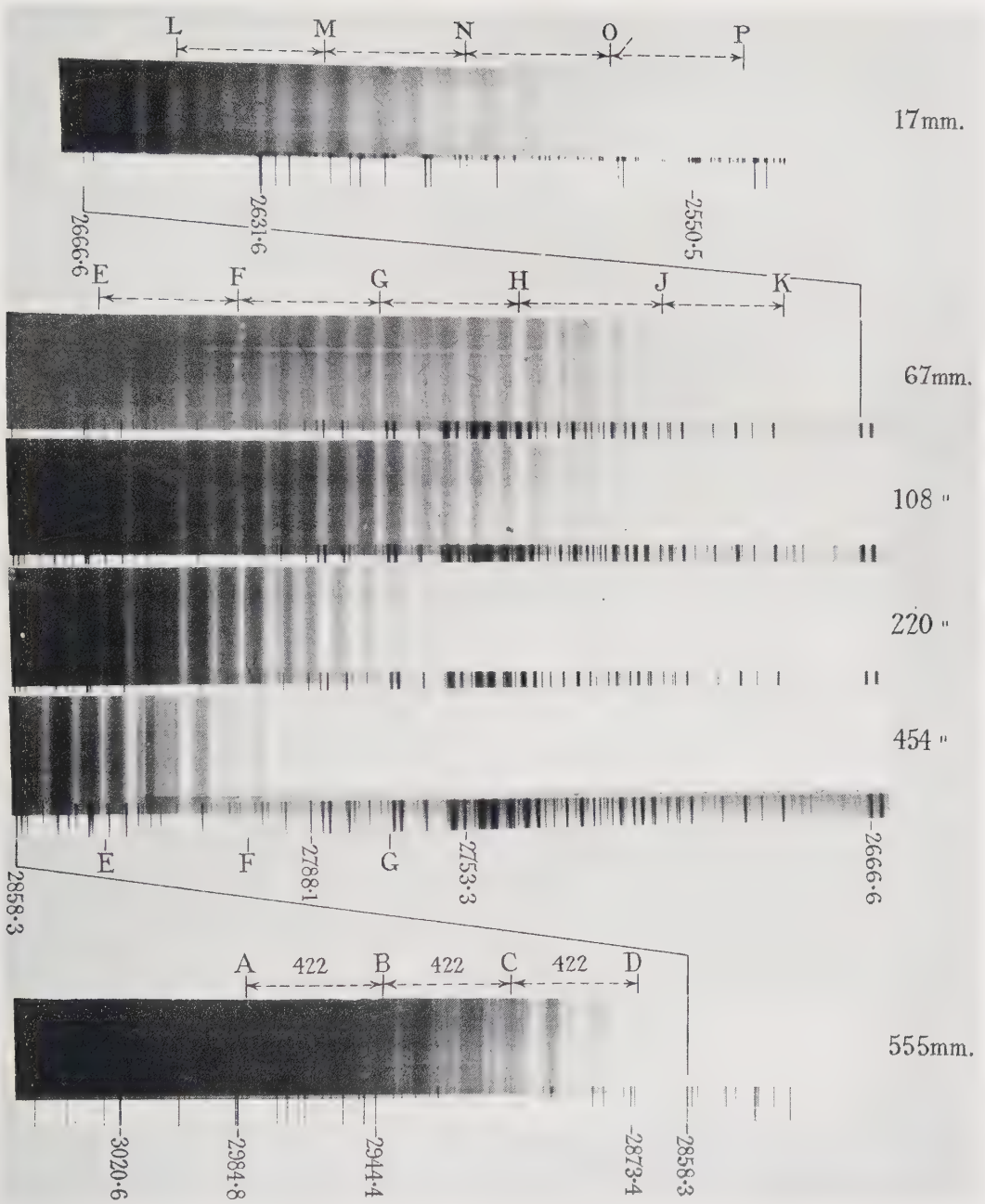
[Plates 4, 5.]

1. *Experimental.*

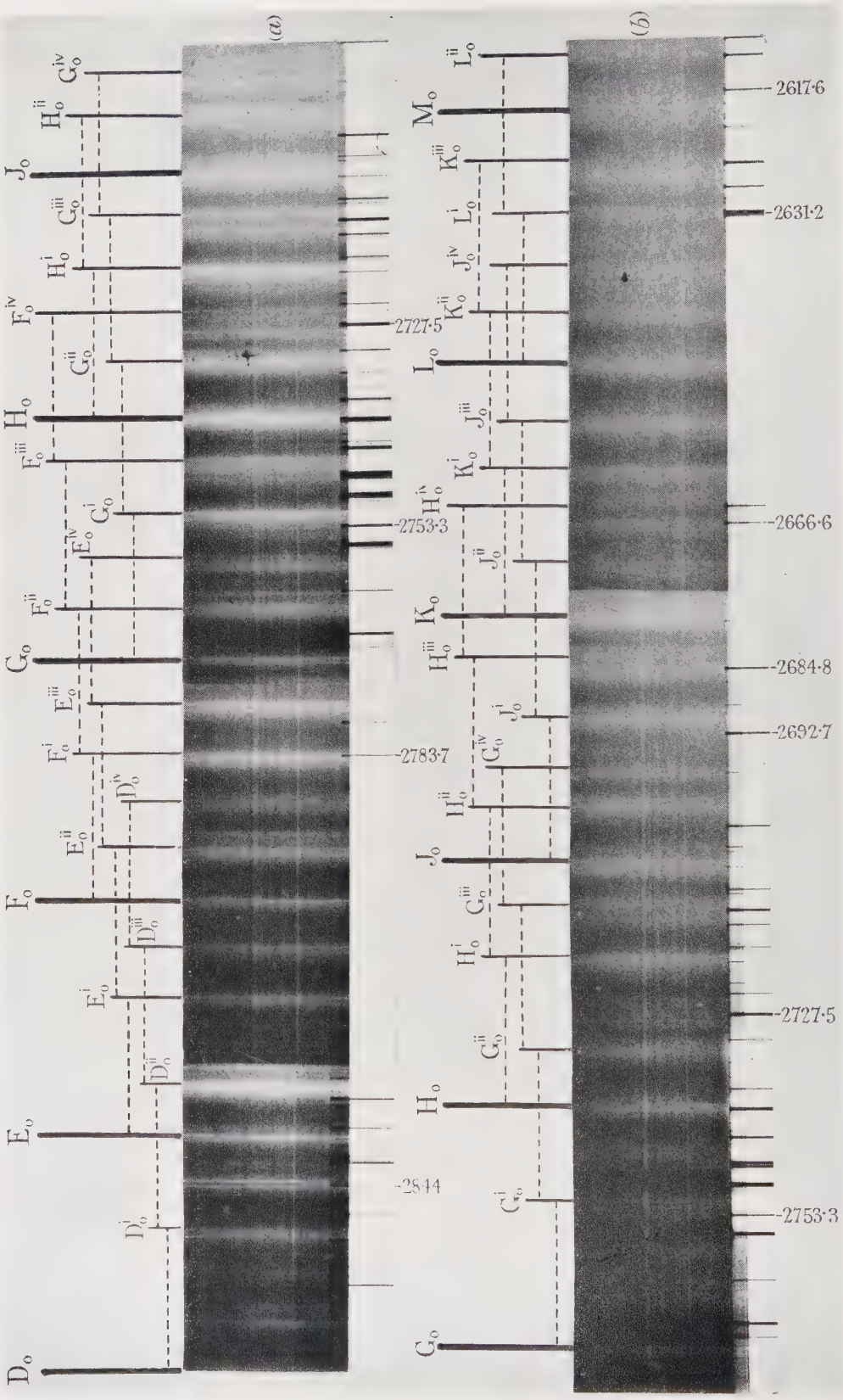
The phosgene used was Kahlbaum's purest and was first fractionally distilled. Two double-necked bulbs, each of about 50 c.c. capacity, were sealed together with a tap between. The free limb of the second bulb was also provided with a tap and connected to two Langmuir pumps in series. The phosgene was cooled in solid carbon dioxide and ether and about 10 c.c. was transferred to the first bulb which was similarly cooled and which was then sealed off. The second bulb was evacuated, put in connection with the first bulb until full of vapour and then evacuated again. This was repeated several times until about 2 or 3 c.c. of phosgene had disappeared. The second bulb was then cooled with solid carbon dioxide and ether and the first bulb allowed to warm slowly until about a third of the phosgene remaining had distilled over. The second bulb was then sealed off from the first and was connected at D to the absorption apparatus shown in fig. 2.

The absorption tube itself consists of a glass tube TT fitted by means of ground joints with two end pieces EE for convenience in cleaning. The total length is 100 cm. The end pieces are provided with polished quartz windows QQ fitted on with cement. The tube is in connection with two bulbs ; a small one S of about 20 c.c. capacity and a large one L of about 500 c.c. These bulbs are connected to one another and to a mercury manometer M by which the pressure in the tube may be registered. The storage bulb G is attached by means of a mercury sealed joint J.

The method of manipulation is as follows. With tap g closed, the whole apparatus is evacuated through V by means of two Langmuir pumps in series, a vacuum of less than 1/1000 mm. being thus obtained. The tap h is then


L
M
N
O
P
17mm.
2666·6
2631·6
2550·5
E
F
G
H
J
K
67mm.
108 "
220 "
454 "
E
F
G
2858·3
2788·1
2753·3
2666·6
A
422
B
422
C
422
D
555mm.
3020·6
2984·8
2944·4
2873·4
2858·3

(*Facing p.* 16 .)


(a)
(b)
2727·5
2753·3
2783·7
2844
2617·6
2631·2
2666·6
2684·8
2692·7
2727·5
2753·3

closed and *g* opened, whereby the reservoir G is filled with vapour from the phosgene bulb. This is repeated several times and then a few cubic centi-

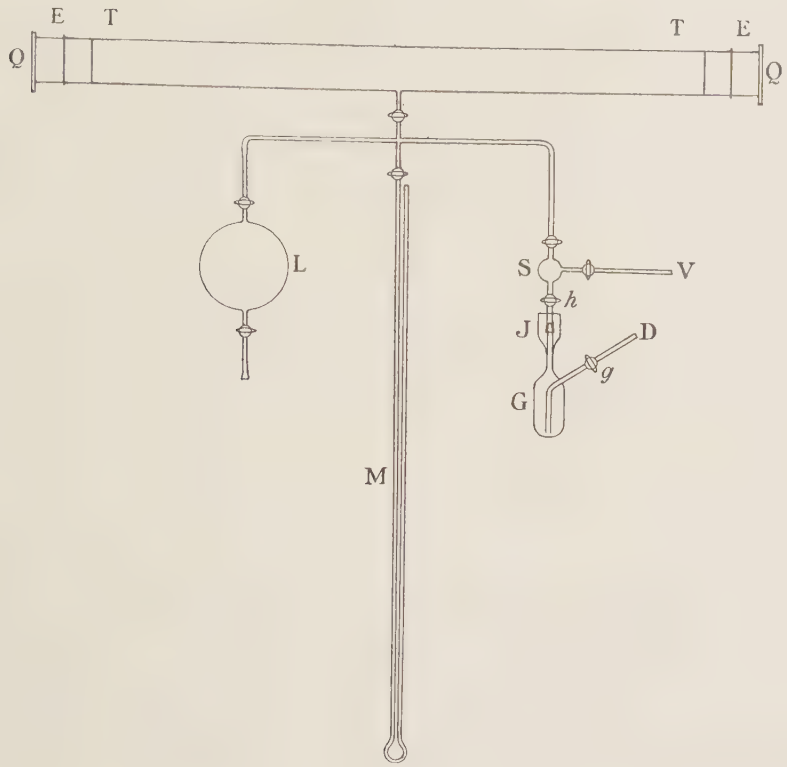


Fig. 2.

metres of liquid are distilled over into G by immersing it in a freezing mixture. Taps *g* and *h* are closed and the rest of the apparatus is again thoroughly evacuated. Any desired quantity of vapour can then be admitted into the absorption tube by opening G to S, then S to L, and finally L to the tube.

Exposures are first made with a very small pressure of vapour and then with a series of increasing pressures. The pressures employed for phosgene varied from 0·1 up to 680 mm. of mercury.

The source of ultra-violet light was a strong high-frequency spark between copper or aluminium electrodes under water, details of which have already been published.*

The comparison spectrum was from a condensed iron spark with self induction as recommended by Hemsalech, which gives very fine lines. The spectra

* Henri and de Làszlô, ' Roy. Soc. Proc.,' A, vol. 105, p. 662 (1924).

were photographed on a Hilger E_1 spectrograph. The time of exposure was about 10 minutes for the absorption spectra and 10 to 30 seconds for the iron spectra.

The absorption spectra were measured directly on the plates by means of a Jobin comparator and also with a Zeiss microscope micrometer attachment. They were also measured with a rule on photographic enlargements made with a very accurately corrected objective. The measurements by these three methods agreed to within one wave number. The wave-lengths are expressed in international Ångström units in air and the wave-numbers are reduced to vacuo and expressed in $cm.^{-1}$.

Accurate measurements of intensities and of separations between certain lines have also been made by microphotometric registration of the spectrum with the Moll's microphotometer of Kipp and Zonen (model 1929). Some of these photomicrograms are reproduced in figs. 1 (p. 181), 3 and 4 (p. 196).

2. *General Description of the Absorption Spectrum.*

The absorption spectrum of phosgene is composed of about 270 bands distributed between 3050 and 2380 A. These bands are not all present at the same time. At low pressures of 1 or 2 mm., only those bands in the extreme ultra-violet between 2500 and 2380 A. make their appearance. Beyond 2380 A. the absorption is continuous and becomes increasingly great towards the region of shorter wave-length. At a pressure of 4 mm. a whole series of bands appear between 2850 and 2600 A., those on the ultra-violet side being stronger than those on the red. As the pressure is further increased, the bands become stronger and stronger; those towards the ultra-violet fuse together while new bands make their appearance towards the red. This continues until at 680 mm. bands are obtained between 3050 and 2380 A. Beyond 2380 A. absorption is complete.

The change in the extent of the absorption with pressure is illustrated in Table II. Column 1 gives the pressure of vapour with a thickness of 100 cm.; column 2 indicates the molecular concentration of vapour calculated from the formula $C = p/22{\cdot}4 \times 760$; column 3 shows the value of 1/100 C, which is a measure of the increase of the intensity of absorption; column 4 gives the limits within which bands appear and the approximate position of the bands; column 5 shows the region beyond which complete absorption begins.

The absorption spectrum of phosgene has a very characteristic appearance shown in the photographic reproduction in Plate 4. Enlargements of a portion

Table II.

Pressure. mm.	Molecular concentration $c = p/22{\cdot}4 \times 760$.	Intensity of absorption. 1/100 C.	Bands present.	General absorption from λ
0·1	$0{\cdot}06 \times 10^{-4}$	—	None	—
0·3	0·18	—	None	—
0·6	0·35	—	None	—
1·4	0·82	122	M to R	<2349
4	2·35	42	E ,, U	2380
8	4·70	21	E ,, Q	2520
17	9·99	10	E ,, O	2550
25	14·69	6·8	E ,, L	2615
48	28·20	3·6	D ,, K	2680
67	39·36	2·6	D ,, K	2680
83	48·75	2·04	D ,, J	2700
125	73·43	1·37	C ,, H	2720
166	97·51	1·03	C ,, H	2730
375	220·2	0·45	B ,, F	2820
555	326·0	0·30	A ,, E	2850
680	399·5	0·25	A ,, D	2880

of this spectrum: (*a*) from $\lambda = 2863$ to 2693 A., and (*b*) from $\lambda = 2770$ to 2614 A., are given in Plate 5.

The spectrum is composed of a large number of intense doublets, and sometimes triplets, distributed at approximately regular intervals of about 9 to 12 A. Between these doublets are many fainter lines irregularly distributed. The microphotogram (fig. 1) shows the structure of a portion of the spectrum, the corresponding bands being indicated in Plate 5 (*a*).

The separation of these doublets in the region of 2800 A. (fig. 1) is about 0·8 to 1·0 A.

The bands of which the doublets are composed are fairly fine and their positions can be determined to within one or perhaps two wave-numbers. They have a sharp edge on the ultra-violet side and are degraded towards the visible side (fig. 1). At wave-lengths less than 2750 A. the bands become less sharp; they grow broader and the edges become more indefinite and diffuse. The further they occur in the ultra-violet, the more diffuse are the bands, and beyond 2650 A. it is impossible to distinguish the doublets. The bands are then about 1 to 2 A. broad, and beyond 2550 A. they exceed 3 A. in breadth. Although they are diffuse, their distribution remains regular.

This broadening is clearly visible in the photographic reproduction (Plate 5 (*b*)) and also in figs. 3 and 4, which are photomicrograms of the sharp doublets No. 151, 152 ($1/\lambda = 36073$ and 36082, Band G_0) and (on the same

scale) of the diffuse band No. 230 ($1/\lambda = 37665$). In fig. 4, the irregularities are due to the grains of the photographic plate.

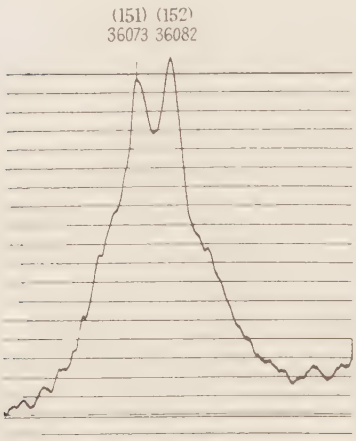


Fig. 3.

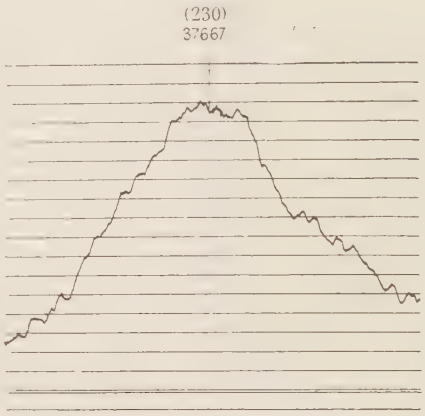


Fig. 4.

4. *Analysis of the Absorption Spectrum.*

The absorption spectrum is composed of a series of groups of bands distributed at regular intervals. Each of these groups is composed of six or seven intense doublets and a number of isolated lines. The groups are almost identically superposable, the period being about 422 cm.$^{-1}$. The spectrum may thus be divided into 11 or 12 successive groups, and these are designated by the letters A_0, B_0, C_0, etc., beginning at the red end. The interval between corresponding bands in each of these groups is constant at 422 cm.$^{-1}$ for the first seven groups, but it decreases in the region where the bands begin to become diffuse (region of predissociation).

There is therefore a principal fundamental vibration period of 422 corresponding to certain atomic vibrations in the phosgene molecule.

Table III gives the positions of the intense bands which have been chosen as origins for the different groups and also the intervals between the origins.

Since the groups are arranged at intervals of 422 cm.$^{-1}$ from the visible towards the ultra-violet, it follows that this interval is due to a vibration period in the activated molecule. This period is designated $\alpha' = 422$ cm.$^{-1}$.

It is then found that from the head of each group, four or five strong bands occur at a constant interval of 254 cm.$^{-1}$ towards the ultra-violet. This interval must, therefore, also be due to a vibration period in the activated molecule. It is designated $\beta' = 254$ cm.$^{-1}$.

Table III.

Group origins.	p'.	λ (air	$1/\lambda$ (vac.).	Interval.
		A.	cm.$^{-1}$.	cm.$^{-1}$.
A_0	0	2979·7	33551	
B_0	1	2942·7	33973	422
C_0	2	2906·5	34395	422
D_0	3	2871·3	34817	422
E_0	4	2836·9	36239	422
F_0	5	2803·4	35661	422
G_0	6	2770·6	36082	421
H_0	7	2739·1	36498	416
J_0	8	2708·5	36910	412
K_0	9	2678·4	37325	415
L_0	10	2648·1	37751	426

The corresponding bands are designated A_0^{i}, A_0^{ii}, A_0^{iii}, A_0^{iv}, B_0^{i}, B_0^{ii} .... These bands are marked on the photograph, Plate 5. Table IV contains the observed wave-numbers and the corresponding differences. The mean value is 254 cm.$^{-1}$.

Table IV.

A_0	—		A^{i}	—		A^{ii}	34056		A^{iii}	—	A^{iv}	34567
									511 = 2 ×	*255*		
B_0	—		B^{i}	34227	*253*	B^{ii}	34480	*260*	B^{iii}	34740	*248*	B^{iv}	34988
C_0	34395	*254*	C^{i}	34649	*253*	C^{ii}	34902	*255*	C^{iii}	35157	*256*	C^{iv}	35413
D_0	34817	*255*	D^{i}	35072	*251*	D^{ii}	35323	*257*	D^{iii}	35580	*253*	D^{iv}	35833
E_0	35239	*253*	E^{i}	35492	*256*	E^{ii}	35748	*253*	E^{iii}	36001	*256*	E^{iv}	36257
F_0	35661	*254*	F^{i}	35915	*254*	F^{ii}	36169	*255*	F^{iii}	36424	*255*	F^{iv}	36679
G_0	36082	*252*	G^{i}	36334	*258*	G^{ii}	36592	*254*	G^{iii}	36846	*256*	G^{iv}	37092
H_0	36498	*255*	H^{i}	36753	*252*	H^{ii}	37005	*255*	H^{iii}	37260		H^{iv}	—
J_0	36910	*255*	J^{i}	37165	*248*	J^{ii}	37413	*252*	J^{iii}	37665		J^{iv}	—

Similarly, from each group head, but now towards the red, there is a series of two or three fainter lines at a constant interval of 302 cm.$^{-1}$. This interval is therefore due to a vibration period in the normal molecule, and as it corresponds to β' it is designated $\beta_0 = 302$ cm.$^{-1}$.

It was difficult to find the vibration frequency α_0 in the normal molecule corresponding to α' in the activated molecule, but the study of the Raman spectrum proved of great assistance in deciding its value.

Since the bands are all degraded towards the visible, the frequency α_0 must be higher than $\alpha' = 422$. The Raman spectrum contains two lines, $a = 567$, and $c = 290$ cm.$^{-1}$. The accuracy of these measurements is not very high and it is therefore probable that a is a harmonic of c. The expected value of α_0 is therefore equal to or slightly greater than that of a or $2c$. Now there are two or sometimes three bands towards the red from each origin A_0, B_0, C_0, ... at a constant interval equal to 582 cm.$^{-1}$. We therefore accept this frequency as the value of α_0.

The absorption spectrum of phosgene is therefore characterised by two pairs of vibration periods : 582 and 302 cm.$^{-1}$ for the normal molecule and 422 and 254 cm.$^{-1}$ for the activated molecule.

From the analysis of the spectrum it follows that the normal molecule of phosgene has three energy levels separated by intervals of 592 cm.$^{-1}$. The bands A_0, B_0, C_0, ... are the strongest. From these origins, there are two bands towards the red at the distance equal to 582 cm.$^{-1}$, but there are no bands at the same interval towards the ultra-violet. It follows that the majority of the molecules are in the zero state ($p_0 = 0$ or possibly $\frac{1}{2}$) and the other vibration states of the normal molecule correspond to $p_0 = 1$ and 2 (or $1\frac{1}{2}$ and $2\frac{1}{2}$).

In conjunction with each of the vibration states of frequency α_0 are those of frequency $\beta_0 = 302$ cm.$^{-1}$. There are three such levels and the corresponding quantum states are denoted by $q_0 = 1$, 2 and 3. The bands are most intense for $q_0 = 1$, feebler and often non-existent for $q_0 = 2$ and 3.

The activated molecule possesses two vibration periods whose quantum numbers are denoted by p' and q'. p' possesses all the values from 0 to 11 and q' from 0 to 6.

When p' is not greater than 6, the corresponding bands are fine with sharp edges. When $p' = 7$ (group H ; $\lambda = 2740$) the bands begin to become diffuse and their positions cannot be determined with an accuracy greater than 3 cm.$^{-1}$. With p' greater than 7, the bands get more and more diffuse until for $p' = 11$ (group M ; $\lambda = 2615$) the width of the band is about 26 to 30 cm.$^{-1}$, and it is impossible to indicate the exact position of the head of the group (Plate 5 (*b*) and fig. 4).

The general structure of the absorption spectrum of phosgene can be illustrated by the schematic representation shown in fig. 5.

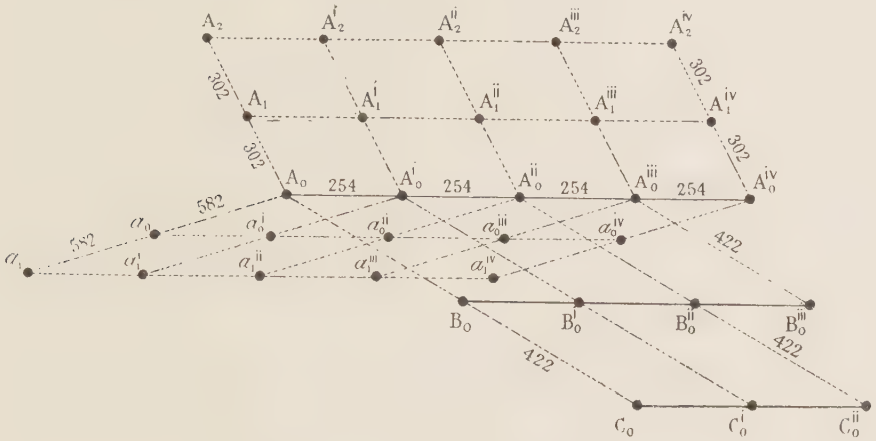


Fig. 5.

The general formula representing the whole band system is :—

$$1/\lambda = 33551 + 422p' - 582p_0 + 254q' - 302q_0$$

or

$$1/\lambda = 33655 + 422\,(p' + \tfrac{1}{2}) - 582\,(p_0 + \tfrac{1}{2}) + 254\,(q' + \tfrac{1}{2}) - 302\,(q_0 + \tfrac{1}{2}).$$

This formula may be written for easier calculation :

$$1/\lambda = 33551 + 422\,(p' - p_0) - 160p_0 + 254\,(q' - q_0) - 48q_0.$$

Table V gives a complete list of all the bands which have been measured, the observed and calculated wave-numbers and the values of p_0, q_0, p' and q' for each band. The intensities are on an arbitrary scale from 0 to 10 and were estimated from three different plates at 555, 166 and 67 mm. ; bands up to number 39 from the first, up to number 90 from the second and the remainder from the third.

Table V.

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
1	32869	—	—	—	—	—	4	—
2	33097	33101	2	1	0	4	3	—
3	33250	33249	0	1	0	0	0	A_1
		33247	1	3	1	3	—	b_3^{iii}
4	33304	33303	2	2	3	1	1	—
5	33329	33329	1	3	3	0	5	d_3
6	33347	33343	1	1	1	1	2	b_1^{i}
		33351	2	1	3	0	—	—
7	33489	33489	0	3	2	0	1	C_3

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
8	33531	—	—	—	—	—	0	—
ν_0	—	33551	0	0	0	0	—	A_0
9	33566	—	—	—	—	—	3	—
10	33594	33597	1	1	1	2	4	b_1^{ii}
		33591	2	3	5	0	—	—
		33595	2	3	2	5	—	—
11	33647	33645	1	0	1	1	1	b_0^{i}
		33643	2	2	2	4	—	—
12	33721	33717	1	2	2	2	2	c_2^{ii}
		33725	2	2	4	1	—	—
13	33751	33751	1	3	4	0	2	e_3
14	33762	33765	1	1	2	1	4	c_1^{i}
		33763	2	3	3	4	—	—
15	33773	33773	2	1	4	0	6	—
		33777	2	1	1	5	—	—
16	33783	—	—	—	—	—	—	—
17	33792	33791	0	2	2	0	2	C_2
18	33898	33899	1	0	1	2	4	b_0^{ii}
		33897	2	2	2	5	—	—
19	33911	33911	0	3	3	0	1	D_3
20	33925	33925	0	1	1	1	5	B_1^{i}
		33923	1	3	2	4	—	c_3^{iv}
—	—	33973	0	0	1	0	—	B_0
21	33988	33985	1	0	0	4	1	a_0^{iv}
22	34023	34019	1	1	2	2	6	c_1^{ii}
23	34030	34027	2	1	4	1	0	—
24	34037	—	—	—	—	—	3	—
25	34056	34059	0	0	0	2	1	A_0^{ii}
		34053	1	2	4	0	—	e_2
		34057	1	2	1	5	—	b_2^{v}
26	34069	34067	1	0	2	1	6	c_0^{i}
		34065	2	2	3	4	—	—
27	34073	34075	2	0	4	0	1	—
28	34139	34139	1	2	3	2	1	d_2^{ii}
29	34148	34147	2	2	5	1	5	—
30	34178	34179	0	1	1	2	6	B_1^{ii}
		34177	1	3	2	5	—	c_3^{v}
31	34182	34187	1	1	3	1	1	d_1^{i}
		34185	2	3	4	4	—	—
32	34194	34191	2	1	5	0	0	—
33	34206	—	—	—	—	—	2	—
34	34223	—	—	—	—	—	—	—
35	34227	34227	0	0	1	1	5	B_0^{i}
		34225	1	2	2	4	—	c_2^{iv}
36	34239	34239	1	0	0	5	1	a_0^{v}
		34235	1	0	3	0	—	d_0
37	34266	34265	0	1	0	4	1	A_1^{iv}
		34266	2	3	6	1	—	—
38	34292	—	—	—	—	—	1	—
39	34305	34307	1	2	4	1	1	e_2^{i}
40	34321	34321	1	0	2	2	5	c_0^{ii}
		34319	2	2	3	5	—	—
41	34327	34329	2	0	4	1	5	—
42	34353	34355	1	1	4	0	8	e_1
		34353	2	3	5	3	—	—

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
43	34374	—	—	—	—	—	5	—
44	34395	34395	0	0	2	0	2	C_0
		34393	1	2	3	3	—	d_2^{iii}
45	34425	34427	1	3	5	1	3	f_3^{i}
46	34444	34441	1	1	3	2	4	d_1^{ii}
		34449	2	1	5	1	—	—
47	34469	34467	0	2	3	1	7	D_2^{i}
48	34480	34481	0	0	1	2	9	B_0^{ii}
		34479	1	2	2	5	—	c_2^{v}
49 *a*	34490	34489	1	0	3	1	—	d_0^{i}
49 *b*	34498	34497	2	0	5	0	3	—
50	34506	34505	0	3	2	4	6	C_3^{iv}
51	34530	34527	1	1	2	4	1	c_1^{iv}
52	34560	34561	1	2	4	2	1	e_2^{ii}
53	34567	34567	0	0	0	4	6	A_0^{iv}
		34568	2	2	6	1	—	—
54	34576	34575	1	0	2	3	8	c_0^{iii}
55	34584	34587	0	3	4	1	2	E_3^{i}
		34583	2	0	4	2	—	—
56	34609	34609	1	1	4	1	8	e_1^{i}
		34607	2	3	5	4	—	—
57	34617	34616	2	1	6	0	4	—
58	34624	34621	2	1	3	5	5	—
59 *a*	34634	34635	0	2	4	0	4	E_2
59 *b*	34639	34639	0	2	1	5	—	B_2^{v}
60	34649	34649	0	0	2	1	3	C_0^{i}
		34647	1	2	3	4	—	d_2^{iv}
61	34657	34657	1	0	4	0	5	e_0
		34655	2	2	5	3	—	—
62	34716	—	—	—	—	—	3	—
63	34725	34721	0	2	3	2	6	D_2^{ii}
		34729	1	2	5	1	—	f_2^{i}
64	34740	34735	0	0	1	3	2	B_0^{iii}
		34741	2	2	4	5	—	—
65	34746	34743	1	0	3	2	5	d_0^{ii}
66	34756	34755	0	3	5	0	4	F_3
		34759	0	3	2	5	—	C_3^{v}
67	34768	34769	0	1	3	1	5	D_1^{i}
		34767	1	3	4	4	—	e_3^{iv}
68	34801	—	—	—	—	—	1	—
69	34813	34815	1	2	4	3	2	e_2^{iii}
70	34817	34817	0	0	3	0	5	D_0
		34815	1	2	4	3	—	—
71	34821	34821	0	0	0	5	2	A_0^{v}
		34822	2	2	6	2	—	—
72	34833	34829	1	0	2	4	2	c_0^{iv}
		34837	2	0	4	3	—	—
73	34845	34848	1	3	6	1	2	g_3^{i}
74	34854	34855	0	1	2	3	2	C_1^{iii}
75	34863	34863	1	1	4	2	2	e_1^{ii}
		34861	2	3	5	5	—	—
76	34872	34870	2	1	6	1	1	—
77	34891	34889	0	2	4	1	1	E_2^{i}
78	34902	34903	0	0	2	2	8	C_0^{ii}
		34901	1	2	3	5	—	d_2^{v}

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
79	34910	34911	1	0	4	1	10	e_0^{i}
		34909	2	2	5	4	—	—
80	34936	34937	0	1	4	0	7	E_1
		34935	1	3	5	3	—	f_3^{iii}
		34936	2	3	7	2	—	—
81	34962	—	—	—	—	—	1	—
82	34976	34975	0	2	3	3	2	D_2^{iii}
83	34988	34989	0	0	1	4	4	B_0^{iv}
		34984	2	2	7	1	—	—
84	34997	34997	1	0	3	3	6	d_0^{iii}
85	35029	35031	1	1	5	1	7	f_1^{i}
		35032	2	1	7	0	—	—
		35028	2	3	6	4	—	—
86	35042	35043	2	1	4	5	1	—
87	35058	35057	0	2	5	0	3	F_2
88	35061	35061	0	2	2	5	6	C_2^{v}
89	35067	35069	1	2	4	4	3	e_2^{iv}
90	35072	35071	0	0	3	1	5	D_0^{i}
91	35140	35143	0	2	4	2	1	E_2^{ii}
		35142	2	2	8	0	—	—
92	35149	35150	1	2	6	1	6	g_2^{i}
93	35157	35157	0	0	2	3	8	C_0^{iii}
94	35169	35165	1	0	4	2	2	e_0^{ii}
		35172	2	0	6	1	—	—
95	35191	35191	0	1	4	1	3	E_1^{i}
		35189	1	3	5	4	—	f_3^{iv}
		35195	2	1	5	0	—	—
		35190	2	3	7	3	—	—
96	35220	—	—	—	—	—	1	—
97	35231	35229	0	2	3	4	3	D_2^{iv}
98	35239	35239	0	0	4	0	8	E_0
		35237	1	2	5	3	—	f_2^{iii}
		35238	2	2	7	2	—	—
99	35259	35259	2	0	5	3	2	—
		35255	2	3	9	0	—	—
100	35274	—	—	—	—	—	1	—
101	35280	35277	0	1	3	3	1	D_1^{iii}
		35282	2	3	6	5	—	—
102	35298	—	—	—	—	—	3	—
103	35309	35311	0	2	5	1	3	F_2^{i}
		35312	1	2	7	0	—	h_2
104	35318	—	—	—	—	—	4	—
105	35323	35325	0	0	3	2	7	D_0^{ii}
		35323	1	2	4	5	—	e_2^{v}
106	35332	35333	1	0	5	1	6	f_0^{i}
		35334	2	0	7	0	—	—
		35330	2	2	6	4	—	—
107	35347	35349	0	3	4	4	2	E_3^{iv}
		35345	2	0	4	5	—	—
		35348	2	3	8	2	—	—
108	35359	35359	0	1	5	0	7	F_1
		35356	1	3	6	3	—	g_3^{iii}
109	35378	35378	2	1	6	3	1	—
110	35395	35397	0	2	4	3	3	E_2^{iii}
111	35402	35404	1	2	6	2	1	g_2^{ii}

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
112	35413	35411	0	0	2	4	1	C_0^{iv}
113	35427	35430	0	3	6	1	2	G_3^{i}
		35426	2	0	6	2	—	—
114	35445	35445	0	1	4	2	2	E_1^{ii}
		35443	1	3	5	5	—	f_3^{v}
		35444	2	1	8	0	—	—
		35444	2	3	7	4	—	—
115	35451	35452	1	1	6	1	2	g_1^{i}
116	35474	35478	0	2	6	0	3	G_2
117	35483	35483	0	2	3	5	8	D_2^{v}
118	35492	35493	0	0	4	1	10	E_0^{i}
		35491	1	2	5	4	—	f_2^{iv}
		35492	2	2	7	3	—	—
119	35502	35500	1	0	6	0	1	g_0
		35505	1	0	3	5	—	d_0^{v}
120	35560	35565	0	2	5	2	1	F_2^{ii}
		35557	2	2	9	0	—	—
121	35570	35566	1	2	7	1	7	h_2^{i}
122	35580	35579	0	0	3	3	9	D_0^{iii}
123	35586	35587	1	0	5	2	1	f_0^{ii}
		35588	2	0	7	1	—	—
		35584	2	2	6	5	—	—
124	35592	35592	0	3	7	0	2	H_3
125	35615	35613	0	1	5	1	1	F_1^{i}
		35614	1	1	7	0	—	h_1
126	35625	35625	1	1	4	5	1	e_1^{v}
127	35648	35650	2	2	8	2	3	—
128	35654	35651	0	2	4	4	6	E_2^{iv}
129	35661	35661	0	0	5	0	10	F_0
		35658	1	2	6	3	—	g_2^{iii}
130	35700	35699	0	1	4	3	1	E_1^{iii}
		35698	2	1	8	1	—	—
		35698	2	3	7	5	—	—
131	35706	35706	1	1	6	2	1	g_1^{ii}
132	35730	35732	0	2	6	1	1	G_1^{i}
133	35736	—	—	—	—	—	6	—
134	35741	35745	1	2	5	5	4	f_2^{v}
135*a*	35748	35747	0	0	4	2	8	E_0^{ii}
		35745	1	2	5	5	—	—
135*b*	35753	35754	1	0	6	1	—	g_0^{i}
136	35778	35780	0	1	6	0	8	G_1
137	35814	35819	0	2	5	3	1	F_2^{iii}
		35811	2	2	9	1	—	—
138	35824	35820	1	2	7	2	1	h_2^{ii}
139	35833	35833	0	0	3	4	7	D_0^{iv}
140	35841	35841	1	0	5	3	5	f_0^{iii}
		35842	2	0	7	2	—	—
141	35892	35894	0	2	7	0	2	H_2
142	35906	35905	0	2	4	5	7	E_2^{v}
		35904	2	2	8	3	—	—
143	35915	35915	0	0	5	1	9	F_0^{i}
		35916	1	0	7	0	—	h_0
144	35938	35938	0	3	6	3	—	G_3^{iii}
		35934	2	0	6	4	—	—
		35935	2	3	10	1	—	—

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
145	35962	35960	1	1	6	3	—	g_1^{iii}
146	35980	35978	1	2	8	1	—	j_2^{i}
		35983	2	2	10	0	—	—
147	35990	—	—	—	—	—	8	—
148	36001	36001	0	0	4	3	10	E_0^{iii}
		36004	0	3	8	0	—	J_3
		36000	2	0	8	1	—	—
		36000	2	2	7	5	—	—
149	36032	36034	0	1	6	1	—	G_1^{i}
150	36064	36065	2	2	9	2	—	—
151	36073	36073	0	2	5	4	8	F_2^{iv}
		36074	1	2	7	3	—	h_2^{iii}
152	36082	36082	0	0	6	0	10	G_0
153	36091	36095	1	0	5	4	—	f_0^{iv}
		36091	1	3	9	1	—	k_3^{i}
154	36147	36148	0	2	7	1	—	H_2^{i}
155	36159	36158	2	2	8	4	7	Diffuse
156	36162	36166	1	2	6	5	2	g_2^{v} diffuse
		36161	2	0	9	0	—	—
157*a*	36169	36169	0	0	5	2	9	F_0^{ii} diffuse
		36170	1	0	7	1	—	h_0^{i}
		36166	1	2	6	5	—	—
157*b*	36175	—	—	—	—	—	—	—
158	36195	36196	0	1	7	0	8	H_1 diffuse
159	36214	36214	1	1	6	4	2	g_1^{iv}
160	36233	36232	1	2	8	2	5	j_2^{ii}
		36237	2	2	10	1	—	—
161	36246	—	—	—	—	—	—	Diffuse
162	36252	36254	2	0	8	2	—	Diffuse
163	36257	36255	0	0	4	4	7	E_0^{iv} diffuse
		36258	0	3	8	1	—	J_3^{i}
164	36307	36306	0	2	8	0	2	J_2
165	36321	36319	2	2	9	3	8	—
166	36334	36336	0	0	6	1	10	G_0^{i}
167	36340	—	—	—	—	—	—	—
168	36391	36393	1	2	9	1	—	k_2^{i}
169	36402	36402	0	2	7	2	3	H_2^{ii}
170	36410	36412	2	2	8	5	5	—
171	36424	36423	0	0	5	3	6	F_0^{iii}
		36424	1	0	7	2	—	h_0^{ii}
172	36449	36450	0	1	7	1	2	H_1^{i}
		36446	0	3	6	5	—	G_3^{v}
173	36460	36460	2	1	8	4	1	—
174	36478	—	—	—	—	—	2	—
175	36487	36486	1	2	8	3	10	j_2^{iii}
176	36498	36498	0	0	7	0	10	H_0 diffuse
177	36515	36512	0	3	8	2	1	J_3^{ii}
178	36518	36516	1	0	6	4	1	g_0^{iv}
		36518	1	3	10	1	—	l_3^{ii}
179	36574	36573	2	2	9	4	4	—
180	36586	36582	1	0	8	1	8	j_0^{i} diffuse
		36587	2	0	10	0	—	—
181	36592	36590	0	0	6	2	—	G_0^{ii} diffuse
182	36609	36608	0	1	8	0	5	J_1 diffuse
		36609	0	3	7	4	—	H_3^{iv}

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
183	36623	36621	2	1	9	3	1	—
184	36631	36630	1	1	7	4	5	h_1^{iv}
185	36643	36647	1	2	9	2	8	k_2^{ii}
186	36666	36669	2	0	9	2	4	—
187	36679	36677	0	0	5	4	6	F_0^{iv}
		36678	1	0	7	3	—	h_0^{iii}
188	36727	—	—	—	—	—	2	From here on all the lines are diffuse
189	36743	36743	1	0	9	0	8	k_0
		36740	1	2	8	4	—	j_2^{iv}
		36745	2	2	10	3	—	—
190	36753	36752	0	0	7	1	10	H_0^{i}
191	36816	36814	0	2	8	2	—	J_2^{ii}
192	36822	36819	1	2	10	1	5	l_2^{i}
193*a*	36833	36836	1	0	8	2	—	j_0^{ii}
193*b*	36846	36844	0	0	6	3	5	G_0^{iii}
		36845	0	3	10	0	—	L_3
194	36857	36853	1	3	9	4	1	k_3^{iv}
195	36890	—	—	—	—	—	4	—
196	36901	36901	1	2	9	3	6	k_2^{iii}
197	36910	36910	0	0	8	0	8	J_0
		36910	0	2	7	4	—	H_2^{iv}
198	36914	—	—	—	—	—	1	—
199	36937	—	—	—	—	—	2	—
200	36940	—	—	—	—	—	1	—
201	36995	36997	1	0	9	1	1	k_0^{i}
		36994	1	2	8	5	—	j_2^{v}
		36999	2	2	10	4	—	—
202	37005	37006	0	0	7	2	6	H_0^{ii}
203	37016	37016	2	0	8	5	8	—
204	37046	37042	1	1	8	4	1	j_1^{iv}
		37047	2	1	10	3	—	—
205	37054	—	—	—	—	—	6	—
206	37069	37068	0	2	8	3	8	J_2^{iii}
207	37077	37073	1	2	10	2	1	l_2^{ii}
208	37092	37098	0	0	6	4	1	G_0^{iv}
		37090	1	0	8	3	—	j_0^{iii}
		37095	2	0	10	2	—	—
209	37113	37116	0	1	8	2	1	J_1^{ii}
210	37137	—	—	—	—	—	1	—
211	37149	37147	0	2	10	0	4	L_2
212	37155	37155	1	2	9	4	6	k_3^{iv}
213	37165	37164	0	0	8	1	8	J_0^{i}
		37165	0	2	7	5	—	H_2^{v}
214	37170	37169	1	0	10	0	1	l_0
215	37243	—	—	—	—	—	—	—
216	37260	37260	0	0	7	3	4	H_0^{iii}
217	37273	37277	0	1	9	1	6	K_1^{i}
		37274	0	3	8	5	—	J_3^{v}
218	37308	—	—	—	—	—	—	—
219	37316	—	—	—	—	—	—	—
220	37325	37325	0	0	9	0	—	K_0
		37322	0	2	8	4	—	J_2^{iv}

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
		37327	1	2	10	3	—	l_2^{iii}
221	37353	37352	0	0	6	5	—	G_0^{v}
		37353	0	3	10	2	—	L_3^{ii}
		37349	2	0	10	3	—	—
222	37399	37401	0	2	10	1	—	L_2^{i}
223	37413	37418	0	0	8	2	—	J_0^{ii}
		37409	1	2	9	5	—	k_2^{v}
224	37423	37423	1	0	10	1	—	l_0^{i}
225	37489	—	—	—	—	—	—	—
226	37527	37531	0	1	9	2	—	K_1^{ii}
227	37555	37555	2	1	10	5	—	—
228	37565	—	—	—	—	—	—	—
229	37579	37579	0	0	9	1	—	K_0^{i}
		37576	0	2	8	5	—	J_2^{v}
230	37665	37672	0	0	8	3	—	J_0^{iii}
231	37724	—	—	—	—	—	—	—
232	37732	—	—	—	—	—	—	—
233	37751	37751	0	0	10	0	—	L_0
234	37810	—	—	—	—	—	—	—
235	37838	37833	0	0	9	2	—	K_0^{ii}
		37835	1	2	10	5	—	l_2^{v}
236	37907	37909	0	2	10	3	—	L_2^{iii}
237	37965	—	—	—	—	—	—	—
238	37987	—	—	—	—	—	—	—
239	38004	38005	0	0	10	1	—	L_0^{i}
240	38037	38039	0	1	9	4	—	K_1^{iv}
241	38080	—	—	—	—	—	—	—
242	38146	—	—	—	—	—	—	—
243	38185	38180	0	0	8	5	—	J_0^{v}
		38185	1	0	10	4	—	l_0^{iv}
244	38246	—	—	—	—	—	—	—
245	38267	—	—	—	—	—	—	—
246	38292	38293	0	1	9	5	—	K_1^{v}
247	38311	—	—	—	—	—	—	—
248	38344	38341	0	0	9	4	—	K_0^{iv}
249	38360	—	—	—	—	—	—	—
250	38383	—	—	—	—	—	—	—
251	38459	—	—	—	—	—	—	—
252	38476	—	—	—	—	—	—	—
253	38543	—	—	—	—	—	—	—
254	38580	—	—	—	—	—	—	—
255	38662	—	—	—	—	—	—	—
256	38730	—	—	—	—	—	—	—
257	38779	—	—	—	—	—	—	—
258	38817	—	—	—	—	—	—	—
259	38886	—	—	—	—	—	—	—
260	38918	—	—	—	—	—	—	—
261	38956	—	—	—	—	—	—	—
262	38994	—	—	—	—	—	—	—
263	39208	—	—	—	—	—	—	—

The agreement between the calculated and observed values is generally very good. As already stated, the value of the interval α' from $p' = 0$ to $p' = 6$ is constant at 422 cm.$^{-1}$, but at $p' = 7$ it begins to diminish. For the calculations of the groups H, J, K, L, the observed values of the origins are accepted and the other bands are calculated from these observed heads.

5. *Theoretical Discussion.*

There are two fundamental frequencies in the absorption of ultra-violet light by phosgene: $\alpha_0 = 582$ and $\beta_0 = 302$ cm.$^{-1}$. The Raman spectrum gives three frequencies: $a = 567$, $b = 444$, and $c = 290$ cm.$^{-1}$. It is probable that the ultra-violet frequency α_0 corresponds to the Raman frequency a and β_0 to c, the Raman frequency 444 being unrepresented in the ultra-violet spectrum.

The infra-red absorption of phosgene in carbon tetrachloride solution has been examined in this laboratory by Mlle. Honneger,* and by Marton.† Six bands were found:—

λ	= 1·11	1·45	1·85	2·40	2·73	4·9 μ
$1/\lambda$	= 9010	6896	5405	4167	3660	2040 cm.$^{-1}$.

Marton (*loc. cit.*) has also examined the infra-red absorption spectrum of phosgene vapour and found the band $\lambda = 2{\cdot}73$ μ. As already mentioned, infra-red measurements are not sufficiently precise to afford accurate information concerning the Raman and ultra-violet frequencies.

It is very difficult to decide to which atoms the different vibration frequencies are due.

For formaldehyde, Henri and Schou (*loc. cit.*) have found two pairs of vibration frequencies:—

α_0	= 1572·3	α'	= 1231·3
β_0	= 441	β'	= 398

For acetaldehyde, Schou (*loc. cit.*) has found that there is only a single pair of frequencies:—

α_0	= 825	α'	= 517

Now for phosgene are found:—

α_0	= 582	α'	= 422
β_0	= 302	β'	= 251

* "Untersuchung über die Absorption ultra-roten Strahlen," 'Dissert.,' Zürich, 1926.
† 'Z. Phys. Chem.,' vol. 117, p. 97 (1925).

It is seen that the vibration frequencies decrease as the vibrating masses increase.

If the first period is due to the vibration of the groups other than the CO, then

for , the frequency $H \longleftrightarrow H = 1572 \cdot 3$ cm.$^{-1}$,

for , the frequency $CH_3 \longleftrightarrow CH = 825$ cm.$^{-1}$,

for , the frequency $Cl \longleftrightarrow Cl = 582$ cm.$^{-1}$.

The frequency β_0 then corresponds to the vibration $C \longleftrightarrow O$. This, however, is hypothesis and can be decided only by further experiments.

It has been found that in the activated molecule, the atomic vibration frequencies are less than those in the normal molecule signifying that the distance between the atoms increases.

It has been shown in the introduction that the *deformability* of a molecule can be measured by the relative variation of the quasi-elastic force between the vibrating atoms. This variation is equal to the value of

$$\frac{\alpha_0^2 - \alpha'^2}{\alpha_0^2} = 0 \cdot 47 \text{ for the vibration } Cl \longleftrightarrow Cl$$

and

$$\frac{\beta_0^2 - \beta'^2}{\beta_0^2} = 0 \cdot 28 \text{ for the vibration } C \longleftrightarrow O.$$

For the molecule of formaldehyde, Henri and Schou have found

$$\frac{\alpha_0^2 - \alpha'^2}{\alpha_0^2} = 0 \cdot 39, \qquad \frac{\beta_0^2 - \beta'^2}{\beta_0^2} = 0 \cdot 12.$$

And for acetaldehyde, this variation is

$$\frac{\alpha_0^2 - \alpha'^2}{\alpha_0^2} = 0 \cdot 61.$$

For the chlorine molecule Kuhn obtained

$$\frac{\alpha_0^2 - \alpha'^2}{\alpha_0^2} = 0 \cdot 90.$$

The molecule of phosgene is, therefore, more deformable than that of formaldehyde, but less than that of chlorine.

The same conclusion is reached from another consideration. The relative variations of the vibration frequencies are approximately equal to the relative variations of the moments of inertia. If the frequencies α_0, α' correspond to the vibration of the Cl-Cl atoms,

$$\frac{\alpha_0 - \alpha'}{\alpha_0} = \frac{J_0 - J'}{J_0} = \frac{582 - 422}{582} = 0{\cdot}28,$$

whereas for formaldehyde, the corresponding value is 0·22.

This great deformability of the phosgene molecule must be connected with the fact that the spectrum becomes diffuse after a small number of vibration states. It has been seen that the bands begin to become diffuse at group H ($p' = 7$) and that the diffusion increases very rapidly towards the ultra-violet.

At about $\lambda = 2700$, all the bands are already diffuse (Plate 5 (*b*)). The region of predissociation therefore begins between 2750 and 2700 A. This change in the character of the spectrum coincides with a diminution of the frequency α' which falls from 422 to 416 and then to 412 cm.$^{-1}$, signifying that, at this stage, the atoms of chlorine are mutually repelled.

It is known that the molecule of phosgene is decomposed by ultra-violet light of wave-length less than $\lambda = 2600$ A., the products being CO and Cl_2, as was first shown by Weigert.* The primary photochemical reaction is, however, not a simple separation of the chlorine molecule from carbon monoxide. We shall try to analyse the mechanism of the photochemical reaction.

The thermal decomposition of phosgene, which proceeds above 350°, has been studied by Christiansen,† and by Bodenstein and his school,‡ and it was found to proceed in stages :

$$COCl_2 \rightarrow COCl + Cl \rightarrow CO + Cl + Cl.$$

The energy of the complete reaction with formation of CO and Cl_2 has been determined by Thomsen (' Thermochem. Untersuchungen,' vol. 2, p. 359) who found the value 26,140 cals., and by Bodenstein and Plaut§ who found 26,200 cals.

The energy of dissociation of Cl_2 into atoms is 57,500 cals. Consequently

* ' Ann. Physique,' vol. 24, p. 55 (1907).

† ' Z. Phys. Chem.,' vol. 103, p. 99 (1923).

‡ ' Z. Phys. Chem.,' vol. 110, p. 399 (1924), vol. 129, p. 241 (1927), vol. 130, p. 422 (1927), vol. 131, p. 153 (1927), and vol. B, 3, p. 459 (1929).

§ ' Z. Phys. Chem.,' vol. 110, p. 399 (1924).

the energy of decomposition of phosgene into normal CO and two atoms of chlorine is :

$$COCl_2 \rightarrow CO + Cl + Cl - 84{,}000 \text{ cals.}$$

It has, however, been shown by Franck and confirmed by a large number of different observers that either one or both atoms produced by the photochemical dissociation of a molecule AB are in an electronically activated state. Heitler and Herzberg† have since shown that in similar cases, the dissociation of a normal molecule by increase of vibration without electronic activation produces one normal and one electronically activated atom, and that the dissociation of an activated molecule produces two normal atoms.

This occurs for example with CN, where we have

$$CN \text{ (normal)} \rightarrow C^* (^5S) + N (^4S)$$

and

$$CN \text{ (activated)} \rightarrow C (^3P) + N (^4S).$$

The direct dissociation of the normal carbon monoxide molecule gives two normal atoms

$$CO \text{ (normal)} \rightarrow C (^3P) + O (^3P)$$

The mechanism of the photochemical dissociation of phosgene is more complicated than that of diatomic molecules. The carbon atom in phosgene is tetravalent, and is therefore in the activated ^5S state. In carbon monoxide it is in the normal ^3P state. The CO group is, therefore, not in the same electronic state in phosgene (or in ketones and aldehydes) as in carbon monoxide. Consequently, the CO molecule combines with chlorine atoms to produce a molecule of phosgene only if it is activated, so that the electronic distribution in the carbon atom corresponds to a ^5S state.

The energy of the primary photochemical action must therefore be written :

$$COCl_2 + \text{light} \rightarrow CO^* + Cl + Cl - (84000 + x),$$

where x is the energy of activation of CO corresponding to the variation of carbon from its ^3P state to its ^5P state :

$$CO^* \rightarrow CO + x.$$

This active state of carbon monoxide is not the experimentally known active state of CO, which corresponds to 48478 cm.$^{-1}$ representing an energy of 140,000 calories, but another very unstable active state, which appears only as an intermediate state in the dissociation of ketones, aldehydes and phosgene.

† 'Z. Physik,' vol. 53, p. 52 (1929), and vol. 57, p. 601 (1929).

The passage of C (^{3}P) to C (^{5}S) corresponds to an energy of about 1·6 volts = 37,000 calories. If the value of x were equal to 37,000 calories the energy of the reaction

$$COCl_2 \rightarrow CO^* + Cl + Cl$$

would be $84{,}000 + 37{,}000 = 121{,}000$ calories. This corresponds to the wave-length $\lambda = 2380$ A., and the absorption in this region is continuous. We have seen, however, that the predissociation of the molecule of phosgene begins at about $\lambda = 2700$ A., which is equivalent to 106,000 calories. If this region corresponds to the limit of photochemical dissociation, then the active CO molecule formed corresponds to the energy :

$$x = 106{,}000 - 84{,}000 = 22{,}000 \text{ calories (1 volt).}$$

It is evident that this value is only a rough approximation, but it gives an order of magnitude which should not be very far from the correct value.

6. *Isotope Effect.*

It is known that the isotope effect appears in molecular spectra both in the rotation spectrum and the vibration spectrum.

The vibrational effect for diatomic molecules is given in a general formula established by Mulliken,† which may be written in the nomenclature already employed :

$$\Delta\nu = (1 - \rho)(p'\alpha' - p_0\alpha_0) - (1 - \rho^2)(x'\alpha'p'^2 - x_0\alpha_0 p_0^2),$$

where $\rho^2 = \mu_1/\mu_2$, μ_1 and μ_2 being the reduced masses of the two isotopes.

For polyatomic molecules the formula must be different, since the vibrations of the different atoms mutually influence each other, and it is certain that for such molecules the value of $\Delta\nu$ should be smaller than that calculated from the Mulliken equation.

In phosgene there are three types of molecules : $COCl^{35}Cl^{35}$ $COCl^{35}C^{37}$ and $COCl^{37}Cl^{37}$, in the ratio 11·3 : 6·7 : 1, since the two isotopes of chlorine exist in the ratio 3·35 : 1.

The bands corresponding to the three molecular isotopes should be distributed as triplets : on the side towards the red, a very feeble band corresponding to the isotopes 37-37, then a stronger one due to the isotopes 37-35, and on the side towards the ultra-violet a very strong band due to the isotopes 35-35.

These are clearly seen in the photomicrograms (figs. 1 and 3).

If the influence of the other atoms be neglected and the frequencies 582 and

† ‘ Phys. Rev.,’ vol. 25, p. 119 (1925).

422 cm.$^{-1}$ attributed to the chlorine atoms only, then (neglecting the band due to 37-37 which is very feeble)

$$1/\mu_2 = \tfrac{1}{35} + \tfrac{1}{35}, \qquad 1/\mu_2 = \tfrac{1}{35} + \tfrac{1}{37},$$

whence $1 - \rho = 0{\cdot}014$.

The values of $\Delta\nu$ calculated from Mulliken's equation for successive value of p' combined with $p_0 = 0$ are given in Table VI.

The separation of the doublets in the phosgene spectrum increases towards the ultra-violet as it should if they are due to isotopes. The observed separations are given in Table VI and it is seen that they are far less than those calculated from the Mulliken formula for a diatomic molecule.

Table VI.—Isotope separation for $p_0 = 0$.

p'.	$\Delta\nu$ calculated for diatomic molecules.	$\Delta\nu$ observed.
0	0	—
1	5·9	Small
2	11·8	3
3	17·7	5
4	23·6	6
5	29·5	8
6	35·4	9
7	—	9·5
8	—	10
9	—	10–12
10	—	13

Summary.

1. The Raman spectrum of phosgene is composed of three lines corresponding to the frequencies :—

$$a = 567 \quad b = 444 \quad c = 290 \text{ cm.}^{-1}.$$

2. The infra-red absorption spectrum of phosgene dissolved in carbon tetrachloride consists of six bands between 1·11 and 4·9 μ. Of these, the bands 1·11, 1·43, 1·77, 2·43 and 4·9 are also found in acetone and acetaldehyde. They are due to the carbonyl group CO. The band 3·1 to 3·2 μ which characterises the group CH is not found in phosgene, but is present in acetone and acetaldehyde.

3. The ultra-violet absorption spectrum of phosgene vapour consists of about 270 bands between 3050 and 2380 A. The absorption region is therefore the same as for all substances containing the carbonyl group. With aldehydes

and ketones, however, the absorption reaches a maximum at about 2800 A., whereas with phosgene it increases continuously towards the ultra-violet.

4. The bands are distributed at regular intervals in the spectrum. These are doublets or triplets with a separation of 0·5 to 1 Å. and also single bands.

5. The separation of the doublets increases towards the ultra-violet. The doublets can be attributed to the isotopes $COCl^{35}Cl^{37}$ and $COCl^{35}Cl^{35}$, the latter giving the more intense band on the ultra-violet side. The separation of the doublets is less than that for the chlorine molecules $Cl^{35}Cl^{37}$ and $Cl^{35}Cl^{35}$.

6. The absorption spectrum of phosgene is a vibration spectrum. The rotation lines are so closely spaced that they cannot be separated. The distribution of the vibration bands is represented very exactly by the formula :

$$1/\lambda = 33551 + 422p' - 582p_0 + 254q' - 302q_0$$

or

$$1/\lambda = 33655 + 422\,(p' + \tfrac{1}{2}) - 582\,(p_0 + \tfrac{1}{2}) + 254\,(q' + \tfrac{1}{2}) - 302\,(q_0 + \tfrac{1}{2}),$$

where $p_0 = 0, 1, 2$, and $q_0 = 0, 1, 2, 3$ are the vibrational quantum numbers of the normal molecule and $p' = 0, 1, 2 \ldots 12$ and $q' = 0, 1, 2, 3, 4, 5$, are those for the activated molecule.

7. The vibration frequencies of the normal molecule are $\alpha_0 = 582$ and $\beta_0 = 302$ cm.$^{-1}$ and those for the activated molecule $\alpha' = 422$ and $\beta' = 254$ cm.$^{-1}$. The values α_0 and β_0 correspond to the frequencies found in the Raman spectrum $a = 567$ and $c = 290$ cm.$^{-1}$.

8. The frequency $\alpha_0 = 582$ is similar to that found for the atoms in the molecule of chlorine, namely, $\alpha_0 = 565$ cm.$^{-1}$. Consequently, α_0 corresponds to the vibration of the chlorine atoms and β_0 to that of the CO group in phosgene.

9. The interval α_0 remains constant up to $p' = 6$, all the corresponding bands being sharp. At $p' = 7$ this interval diminishes and at the same time the bands become diffuse, the molecule being in a state of "predissociation." The distance between vibrating atoms is then increased.

10. The deformability of the molecule of phosgene is greater than that of formaldehyde but less than that of acetaldehyde and chlorine.

11. An activation of about 106,000 calories ($\lambda = 2700$) causes predissociation of phosgene, the bands becoming increasingly more diffuse and broader towards the ultra-violet. The photochemical decomposition of phosgene begins in this region.

12. The initial photochemical dissociation of phosgene is represented by the primary reaction :

$$COCl_2 \rightarrow CO^* + Cl + Cl,$$

with production of active carbon monoxide.

This active state corresponds to an energy of about 22,000 calories. It represents an electronic distribution analogous to that of a carbon atom in the ^5S state.

13. The electronic activation of similarly constituted compounds containing the CO group is :—

Formaldehyde (H_2 . CO)	$\nu_0 = 28280$ cm.$^{-1}$	$E_\epsilon = 80600$ cals.
Acetaldehyde (CH_3H . CO) ..	29409	83800
Propaldehyde (C_2H_5H . CO) ..	29350	83650
Phosgene (Cl_2 . CO)	33655	95900

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